

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



10/536679



(43) International Publication Date
17 June 2004 (17.06.2004)

PCT

(10) International Publication Number
WO 2004/050769 A2

(51) International Patent Classification⁷: C09B 62/44

(21) International Application Number:
PCT/EP2003/050878

(22) International Filing Date:
24 November 2003 (24.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02406046.9 2 December 2002 (02.12.2002) EP

(71) Applicant (for all designated States except US): CIBA
SPECIALTY CHEMICALS HOLDING INC. [CH/CH];
Klybeckstrasse 141, CH-4057 Basel (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): SCHMIEDL,
Jürgen [DE/DE]; Belchenstrasse 17, 79585 Steinen
(DE). SCHOEHN, Damien [FR/FR]; Rue des Sorbiers
7, F-68190 Ensisheim (FR). KOCH, Klaus [DE/CH];
Tramstrasse 35N, CH-4132 Muttenz (CH).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE,
GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,
MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT,
RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

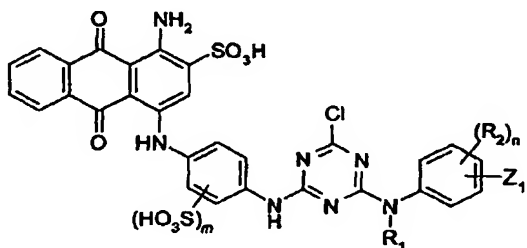
(84) Designated States (*regional*): ARIPO patent (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: REACTIVE DYES, A PROCESS FOR THEIR PREPARATION AND THEIR USE



(1)

(57) Abstract: Reactive dyes of formula (1): wherein R₁, is optionally substituted C₁-C₄ alkyl, R₂ is halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy or sulfo, Z₁ is a radical of formula -SO₂-Y (2a), -CO-NH-(CH₂)_k-SO₂-Y (2b), -NH-CO-CH(Hal)-CH₂-Hal (2c) -NH-CO-C(Hal)=CH₂ or (2d) wherein Hal is chlorine or bromine, Y is vinyl or a radical -CH₂CH₂-U and U is a group removable under alkaline conditions, k is the number 2, 3, 4, 5 or 6, n is the number 0, 1 or 2 and m is the number 0 or 1, are suitable for dyeing or printing cellulose-containing fibre materials, preferably natural or synthetic polyamide fibre materials, and produce, with a high colour yield, dyeings

and prints having good fastness properties.

- 1 -

Reactive dyes, a process for their preparation and their use

The present invention relates to novel reactive dyes, to a process for their preparation and to their use in the dyeing or printing of textile fibre materials.

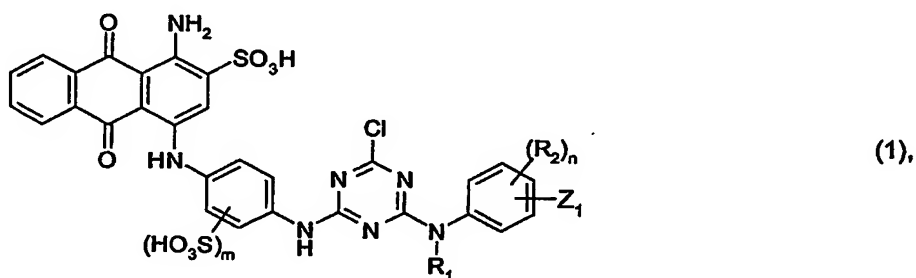
The practice of dyeing using reactive dyes has recently led to higher demands being made on the quality of the dyeings and the profitability of the dyeing process. As a result, there continues to be a need for novel reactive dyes having improved properties, especially in respect of their application.

Dyeing nowadays requires reactive dyes that have sufficient substantivity and at the same time have good ease of washing off of unfixed dye. They should also have a good colour yield and high reactivity, the objective being to provide especially dyeings having high degrees of fixing. The known dyes do not satisfy these requirements in all properties.

The problem underlying the present invention is accordingly to find, for the dyeing and printing of fibre materials, novel improved reactive dyes having the qualities characterised above to a high degree. The novel dyes should especially be distinguished by high fixing yields and high fibre-dye bond stabilities. The dyes should also yield dyeings having good allround properties, for example fastness to light and to wetting.

It has been found that the problem posed is largely solved by the novel dyes defined hereinbelow, especially when the dyes are used for dyeing synthetic polyamide fibre materials.

The present invention therefore relates to reactive dyes of formula



wherein

- 2 -

R_1 is optionally substituted C_1 - C_4 alkyl,

R_2 is halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy or sulfo,

Z_1 is a radical of formula



wherein

Hal is chlorine or bromine,

Y is vinyl or a radical $-\text{CH}_2\text{CH}_2\text{-U}$ and U is a group removable under alkaline conditions,

k is the number 2, 3, 4, 5 or 6,

n is the number 0, 1 or 2 and

m is the number 0 or 1.

The dyes of formula (1) according to the invention are fibre-reactive. Fibre-reactive compounds are to be understood as compounds that are capable of reacting with the hydroxyl groups of cellulose, with the amino, carboxy, hydroxy or thiol groups in wool and silk or with the amino groups and, optionally, with the carboxy groups of synthetic polyamides, to form covalent chemical bonds.

C_1 - C_4 Alkyl R_1 is, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl or isobutyl, preferably methyl or ethyl, especially ethyl. The alkyl radical R_1 is unsubstituted or substituted, for example, by hydroxy, sulfo, sulfato, cyano or by carboxy. The unsubstituted radical is preferred.

As C_1 - C_4 alkyl there come into consideration for R_2 e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and isobutyl, preferably methyl or ethyl, especially methyl.

As C_1 - C_4 alkoxy there come into consideration for R_2 e.g. methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy and isobutoxy, preferably methoxy or ethoxy, especially methoxy.

- 3 -

As halogen there come into consideration for R_2 e.g. fluorine, chlorine and bromine, preferably chlorine or bromine, especially chlorine.

As a group U removable under alkaline conditions there come into consideration e.g. -Cl, -Br, -F, -OSO₃H, -SSO₃H, -OCO-CH₃, -OPO₃H₂, -OCO-C₆H₅, -OSO₂-C₁-C₄alkyl and -OSO₂-N(C₁-C₄alkyl)₂. U is preferably a group of formula -Cl, -OSO₃H, -SSO₃H, -OCO-CH₃, -OCO-C₆H₅ or -OPO₃H₂, especially -Cl or -OSO₃H, more especially -OSO₃H.

Examples of suitable radicals Y are accordingly vinyl, β -bromo- or β -chloro-ethyl, β -acetoxy-ethyl, β -benzyloxyethyl, β -phosphatoethyl, β -sulfatoethyl and β -thiosulfatoethyl. Y is preferably vinyl, β -chloroethyl or β -sulfatoethyl, especially vinyl or β -sulfatoethyl, more especially vinyl.

In the reactive dye of formula (1) according to the invention, R_2 is preferably C₁-C₄alkyl, C₁-C₄alkoxy or sulfo, especially sulfo.

In the reactive dye of formula (1) according to the invention, Hal is preferably bromine.

m is preferably the number 1.

n is preferably the number 0 or 1, especially the number 0.

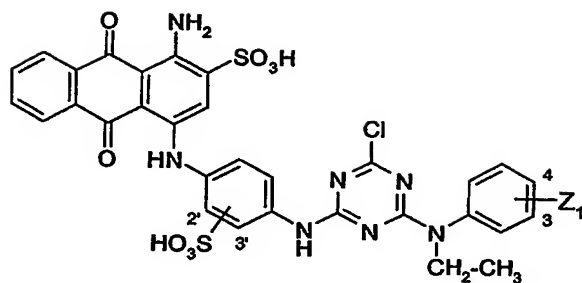
Preferably, m is the number 1 and n is the number 0.

k is preferably the number 2 or 3, especially the number 2.

In the reactive dye of formula (1) according to the invention, Z₁ is preferably a radical of formula (2a) or (2b), especially of formula (2a), the variables having the definitions and preferred meanings given above.

The reactive dye of formula (1) is preferably a dye of formula

- 4 -



(1a),

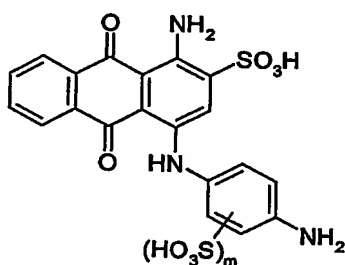
wherein

Z_1 has the definitions and preferred meanings given above, the numbers 2' and 3' indicate the possible bonding positions of the sulfo group and the numbers 3 and 4 indicate the possible bonding positions of Z_1 .

The sulfo group is preferably bonded in the 2'-position.

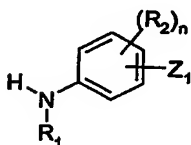
Z_1 is preferably bonded in the 3-position.

The present invention relates also to a process for the preparation of reactive dyes of formula (1), which comprises reacting a compound of formula



(2)

and a compound of formula



(3)

- 5 -

with cyanuric chloride, R_1 , R_2 , Z_1 , m and n having the definitions and preferred meanings given above.

Since the individual process steps can be carried out in different orders, including, if desired, simultaneously, various process variants are possible. The reaction is usually carried out stepwise, the order in which the single reactions between the individual reaction components is carried out advantageously being governed by the particular conditions. For example, about one molar equivalent of an amine of formula (3) is reacted with about one molar equivalent of cyanuric chloride and the resulting product is then condensed with about one molar equivalent of a compound of formula (2). In another process variant, for example about one molar equivalent of a compound of formula (2) is reacted with about one molar equivalent of cyanuric chloride and the resulting mixture is then condensed with about one molar equivalent of an amine of formula (3).

The individual condensation reactions are carried out e.g. in accordance with processes known *per se*, generally in aqueous solution, at a temperature of e.g. from 0 to 50°C, especially from 0 to 10°C, and a pH of e.g. from 1 to 10, especially from 1 to 7.

The end product can optionally also be subjected to a transformation reaction. Such a transformation reaction is, for example, the conversion into its vinyl form of a reactive group in the radical Z_1 that is capable of being vinylated, e.g. by treatment with dilute sodium hydroxide solution, for example the conversion of the β -sulfatoethylsulfonyl or β -chloroethylsulfonyl group into the vinylsulfonyl radical or the conversion of the α,β -dihalopropionylamino group into the α -haloacryloylamino radical. Such reactions are known *per se*. Such a transformation reaction is generally carried out in a neutral to alkaline medium at a temperature of e.g. from 20 to 70°C, at a pH of e.g. from 6 to 14.

The compounds of formulae (2) and (3) are known or can be prepared analogously to known processes.

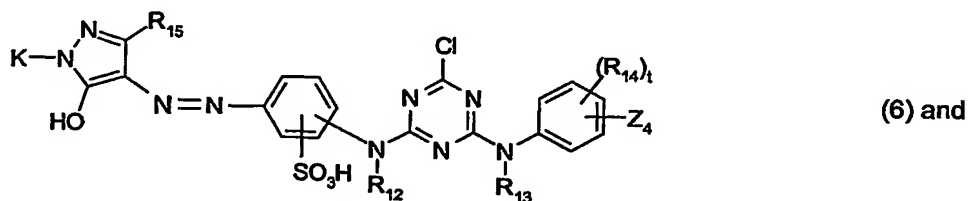
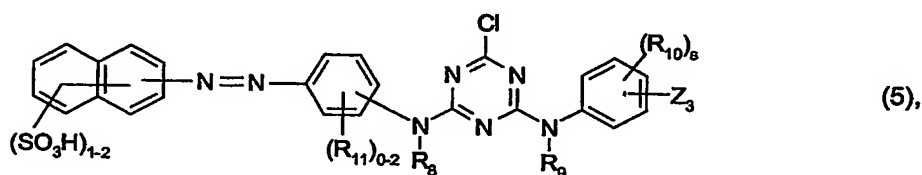
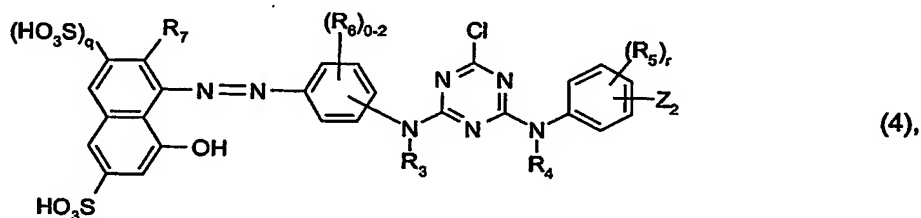
The reactive dyes of formula (1) according to the invention are suitable for dyeing or printing nitrogen-containing or hydroxyl-group-containing fibre materials, paper or leather, e.g. textile fibre materials of cellulose, silk and especially wool or synthetic polyamides.

- 6 -

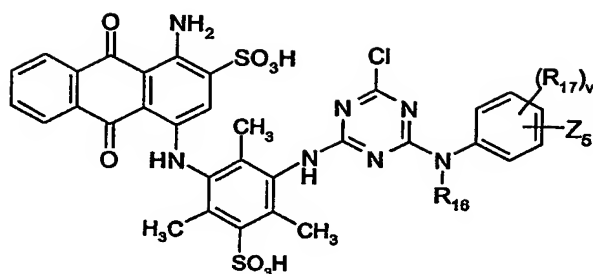
Preference is given to the dyeing or printing of natural or synthetic polyamide fibre materials, especially synthetic polyamide fibre materials.

The reactive dyes of formula (1) yield level, brilliant dyeings having good allround properties, especially good fastness to rubbing, to wetting, to wet rubbing and to light. They are also distinguished by uniform colour build-up, good affinity, high reactivity, good fixing ability and very good build-up ability. The dyes according to the invention have good water-solubility and are readily combinable with other dyes.

The present invention relates also to a process for dyeing or printing hydroxyl-group-containing or nitrogen-containing fibre materials, preferably natural or synthetic polyamide fibre materials and especially synthetic polyamide fibre materials, which process comprises using at least one reactive dye of formula (1), wherein R_1 , R_2 , Z_1 , m and n have the definitions and preferred meanings given above; together with at least one reactive dye selected from the group of formulae



- 7 -



(7).

wherein

R₃, R₄, R₈, R₉, R₁₂, R₁₃ and R₁₆ are each independently of the others hydrogen or unsubstituted or substituted C₁-C₄alkyl,

R₅, R₁₀, R₁₄ and R₁₇ are each independently of the others halogen, C₁-C₄alkyl, C₁-C₄alkoxy or sulfo,

(R₆)₀₋₂ and (R₁₁)₀₋₂ are each independently of the other 0, 1 or 2 substituents selected from the group C₁-C₄alkyl, C₁-C₄alkoxy, C₂-C₄alkanoylamino, ureido, sulfamoyl, halogen, sulfo and carboxy,

R₇ is amino or N-mono- or N,N-di-C₁-C₄alkylamino,

R₁₅ is C₁-C₄alkyl, carboxy, unsubstituted C₁-C₄alkoxy or C₁-C₄alkoxy substituted by carboxy,

K is a phenyl radical, which is substituted by 0, 1, 2 or 3 substituents selected from the group C₁-C₄alkyl, C₁-C₄alkoxy, sulfamoyl, carbamoyl, halogen, sulfo and carboxy, or is a naphthyl radical substituted by 1, 2 or 3 sulfo groups,

Z₂, Z₃, Z₄ and Z₅, each independently of the others, have the definitions given for Z₁,

q is the number 0 or 1, and

r, s, t and v are each independently of the others the number 0, 1 or 2.

The radicals R₃, R₄, R₈, R₉, R₁₂, R₁₃ and R₁₆ as C₁-C₄alkyl radicals are straight-chain or branched. Examples that may be mentioned are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl, preferably methyl and ethyl. The alkyl radicals are unsubstituted or may be further substituted, for example by hydroxy, sulfo, sulfato, cyano or by carboxy. Preferred as substituents are hydroxy, sulfo or sulfato, especially hydroxy or sulfato, more especially hydroxy. The unsubstituted radicals are preferred.

As C₁-C₄alkyl there come into consideration for R₅, R₆, R₁₀, R₁₁, R₁₄, R₁₅ and R₁₇, each independently of the others, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and isobutyl, preferably methyl or ethyl, especially methyl.

- 8 -

As C₁-C₄alkoxy there come into consideration for R₅, R₆, R₁₀, R₁₁, R₁₄, R₁₅ and R₁₇, each independently of the others, e.g. methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy and isobutoxy, preferably methoxy or ethoxy, especially methoxy. The radical R₁₅ may be substituted by carboxy.

As halogen there come into consideration for R₅, R₆, R₁₀, R₁₁, R₁₄ and R₁₇, each independently of the others, e.g. fluorine, chlorine and bromine, preferably chlorine or bromine, especially chlorine.

As C₂-C₄alkanoylamino there come into consideration for R₆ and R₁₁, independently of one another, e.g. acetylamino and propionylamino, especially acetylamino.

As N-mono- or N,N-di-C₁-C₄alkylamino there come into consideration for R₇ e.g. methylamino, ethylamino, n-propylamino, n-butylamino, N,N-dimethylamino and N,N-diethylamino, preferably methylamino, ethylamino, N,N-dimethylamino or N,N-diethylamino, especially methylamino, ethylamino or N,N-dimethylamino.

K as a phenyl radical is unsubstituted or substituted by 1, 2 or 3 substituents selected from the group C₁-C₄alkyl, e.g. methyl or ethyl, preferably methyl; C₁-C₄alkoxy, e.g. methoxy or ethoxy, preferably methoxy; sulfamoyl, carbamoyl, halogen, e.g. bromine, chlorine or fluorine, preferably chlorine; sulfo and carboxy.

K as a naphthyl radical is substituted by 1, 2 or 3, preferably 1 or 2, sulfo groups.

Preferably, the radicals R₃, R₈ and R₁₂ are each independently of the others hydrogen, methyl or ethyl, especially hydrogen.

Preferably, the radicals R₄, R₉, R₁₃ and R₁₆ are each independently of the others hydrogen, methyl or ethyl, especially hydrogen.

In a particular embodiment of the present invention, the radicals R₄, R₉, R₁₃ and R₁₆ are ethyl.

- 9 -

The radicals R_5 , R_{10} , R_{14} and R_{17} each independently of the others have the preferred meanings given above for R_2 .

Preferably, R_8 and R_{11} independently of one another are C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, ureido, sulfo or carboxy, especially C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, ureido or sulfo.

R_8 is especially preferably a sulfo group.

R_{11} is especially preferably a ureido radical or a C_2 - C_4 alkanoylamino radical, more especially a C_2 - C_4 alkanoylamino radical.

R_7 is preferably amino.

K is preferably a phenyl radical substituted by 1, 2 or 3 substituents selected from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen and sulfo, especially halogen and sulfo.

Z_2 , Z_3 and Z_4 , each independently of the others, have the definitions and preferred meanings given above for Z_1 .

In the reactive dye of formula (7), Z_5 is preferably a radical of formula (2a) or (2b), especially of formula (2b), wherein the variables have the definitions and preferred meanings given above.

q is preferably the number 0.

There come into consideration for r , s , t and v , each independently of the others, the definitions and preferred meanings given above for n .

Special preference is given to the process according to the invention in which the reactive dye of formula (1) is a reactive dye of formula (1a) wherein

Z_1 has the definitions and preferred meanings given above and Z_1 and the sulfo group are preferably bonded as indicated above.

- 10 -

Preference is given to the process according to the invention wherein, in the reactive dye of formula (4),

R₃, R₄ and R₅ are each hydrogen, R₆ is a sulfo group, R₇ is amino, Z₂ is a radical of formula (2a) wherein Y is vinyl, and q and r are each the number 0.

Preference is given to the process according to the invention wherein, in the reactive dye of formula (5),

R₈, R₉ and R₁₀ are each hydrogen, R₁₁ is an acetylamino group, Z₃ is a radical of formula (2a) wherein Y is vinyl, and s is the number 0, and the naphthyldiazo component has 2 sulfo groups.

Preference is given to the process according to the invention wherein, in the reactive dye of formula (6),

R₁₂, R₁₃ and R₁₄ are each hydrogen, R₁₅ is methyl, Z₄ is a radical of formula (2a) wherein Y is vinyl, and t is the number 0, and K is a 2,5-dichloro-4-sulfophenyl radical.

Preference is given to the process according to the invention wherein, in the reactive dye of formula (7),

R₁₆ and R₁₇ are each hydrogen, Z₅ a radical of formula (2b) wherein Y is vinyl and k is the number 2, and v is the number 0.

A particular embodiment of the process according to the invention comprises using at least one reactive dye of formula (1) together with a reactive dye of formula (6), wherein R₁, R₂, R₁₂, R₁₃, R₁₄, R₁₅, K, Z₁, Z₄, m, n and t have the definitions and preferred meanings given above.

The above-described embodiment yields brilliant green hues that exhibit scarcely any catalytic fading.

The reactive dyes of formulae (4), (5), (6) and (7) are known or can be prepared analogously to known processes.

The sulfo groups present in the reactive dye of formula (1) according to the invention and in the reactive dyes of formulae (4), (5), (6) and (7) are each either in the form of their free acid

- 11 -

or, preferably, in the form of a salt thereof. Salts that come into consideration include, for example, the alkali metal, alkaline earth metal and ammonium salts, salts of an organic amine and mixtures thereof. Examples that may be mentioned are sodium, lithium, potassium and ammonium salts, the salt of mono-, di- or tri-ethanolamine and Na/Li or Na/Li/NH₄ mixed salts.

The reactive dyes of formula (1) according to the invention and the reactive dyes of formulae (4), (5), (6) and (7) may comprise further additives, e.g. sodium chloride or dextrin.

The process according to the invention and the reactive dyes of formula (1) can be used in accordance with customary dyeing or printing processes. In addition to comprising water and the dyes, the dyeing liquors or printing pastes may comprise further additives, for example wetting agents, anti-foams, levelling agents or agents that influence the properties of the textile material, for example softeners, additives for flame-resistant finishes or dirt-, water- and oil-repellents and also water-softeners and natural or synthetic thickeners, e.g. alginates and cellulose ethers.

The amounts in which the individual dyes are used in the dye baths or printing pastes may vary within wide limits depending on the desired depth of colour; amounts of from 0.01 to 15 % by weight, especially from 0.1 to 10 % by weight, based on the goods to be dyed and the printing paste have proved advantageous.

Printing methods such as, for example, displacement printing or space dyeing are important in the case of carpet fabrics.

Preference is given to dyeing that is carried out especially according to the exhaust method and, in the case of carpet dyeing, it can also be carried out according to the continuous method.

Synthetic polyamide fibres are preferably dyed at a pH value of from 2 to 7, especially from 2.5 to 5.5, more especially from 2.5 to 4. The liquor ratio can be selected from within a wide range, e.g. from 1:5 to 1:50, preferably from 1:5 to 1:30. Dyeing is preferably carried out at a temperature of from 80 to 130°C, especially from 85 to 120°C.

- 12 -

In order to enhance the wet-fastness properties of dyed synthetic polyamide fibres, an aftertreatment can be carried out at a pH value of e.g. from 7 to 12, especially from 7 to 9, and a temperature of e.g. from 30 to 100°C, especially from 50 to 80°C, to remove any unfixed dye. In the case of intense hues, for example in the case of dyeings of very deep colour, especially on fibre blends, unfixed dye can advantageously be removed reductively, by adding to the alkaline aftertreatment bath a reducing agent, for example a hydrosulfite, e.g. sodium hydrosulfite. Dye that has been fixed in the fibre material is not attacked by the treatment. Advantageously, the amount of reducing agent added is e.g. from 0.1 to 6 % by weight, especially from 0.5 to 5 % by weight, based on the weight of the aftertreatment bath.

The reactive dyes used in the process according to the invention are distinguished by uniform colour build-up, good affinity and good fixing ability, good constancy of shade even at different concentrations, good fastness properties and are especially also readily combinable with other dyes. The reactive dyes used in the process according to the invention are advantageously suitable for metamerism control, that is to say, two shades that match in daylight will also match in other light, for example artificial light.

Synthetic polyamide fibre materials suitable for dyeing or printing in accordance with the invention include, for example, polyamide-6 (poly- ϵ -caprolactam), polyamide-6,6 (polyhexamethylenedipamide), polyamide-7, polyamide-6,12 (polyhexamethylenedodecanoamide), polyamide-11 and polyamide-12, copolyamides with polyamide-6,6 or with polyamide-6, e.g. polymers of hexamethylenediamine, ϵ -caprolactam and adipic acid and polymers of adipic acid, hexamethylenediamine and isophthalic acid or of adipic acid, hexamethylenediamine and 2-methylpentamethylenediamine or 2-ethyltetramethylenediamine, and also blend fabrics or mixed yarns of synthetic polyamide and wool.

The process according to the invention and the reactive dyes according to the invention are advantageously suitable also for dyeing or printing microfibres of synthetic polyamides. Microfibres are understood to mean fibre materials constructed from threads having an individual thread fineness of 1 denier (1.1 dTex). Such microfibres are known and are usually produced by melt-spinning.

The said textile material may be in an extremely wide variety of manufactured forms, e.g. in the form of fibres, yarns, woven fabrics or knitted fabrics and in the form of carpets.

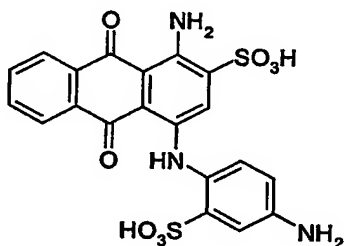
- 13 -

Level dyeings having good allround properties, especially good fastness to rubbing, to wetting, to wet rubbing and to light, are obtained

The following Examples serve to illustrate the invention. The temperatures are given in degrees Celsius. Unless otherwise indicated, parts are parts by weight and percentages relate to percent by weight. Parts by weight relate to parts by volume in the same ratio as kilograms to litres.

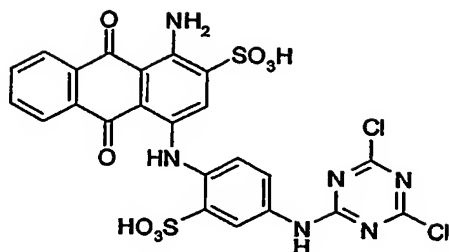
Example 1:

a) 4.7 parts of cyanuric chloride are suspended in the course of from 10 to 15 minutes at a temperature of from 0 to 2°C in 47 parts of ice, 23 parts of water and 0.025 part of $\text{Na}_2\text{HPO}_4 \times 12\text{H}_2\text{O}$. In the course of 45 minutes at a temperature of from 0 to 2°C, a solution of 12 parts of a compound of formula

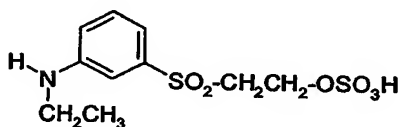


in 150 parts of water and 18.1 parts of an aqueous 2N sodium hydroxide solution is then fed in, the pH being maintained at a value of 5 by the addition of aqueous 2N sodium hydroxide solution. Stirring is then carried out for 40 minutes at a temperature of from 0 to 2°C. A solution is obtained, which comprises the compound, indicated in the form of the free acid, of formula

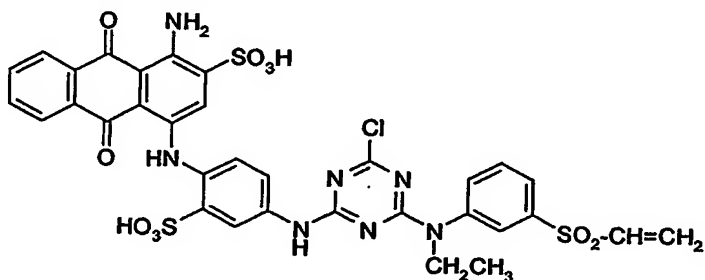
- 14 -



b) 8.2 parts of a compound of formula



are dissolved in 140 parts of water. The resulting solution is added dropwise in the course of 45 minutes to the solution, cooled to a temperature of from 0 to 2°C, obtained according to a). During the addition, the pH is maintained at a value of 6 by means of aqueous 2N sodium hydroxide solution. Stirring is then carried out overnight at a temperature of from 0 to 2°C and a pH value of 6. For the purpose of converting the β -sulfatoethylsulfonyl form into the vinyl form, the pH value is adjusted to 10 using 2N sodium hydroxide solution and stirred for 30 minutes at room temperature. The reaction mixture is then rendered neutral using dilute hydrochloric acid and, after the addition of sodium chloride, is subsequently stirred for one hour in an ice bath. The precipitated dye is filtered off, washed with aqueous sodium chloride solution and dried at a temperature of 40°C. A dye is obtained which, in the form of the free acid, corresponds to the compound of formula



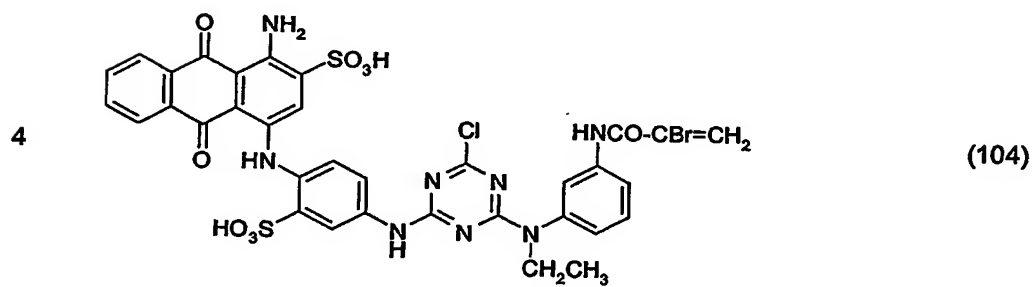
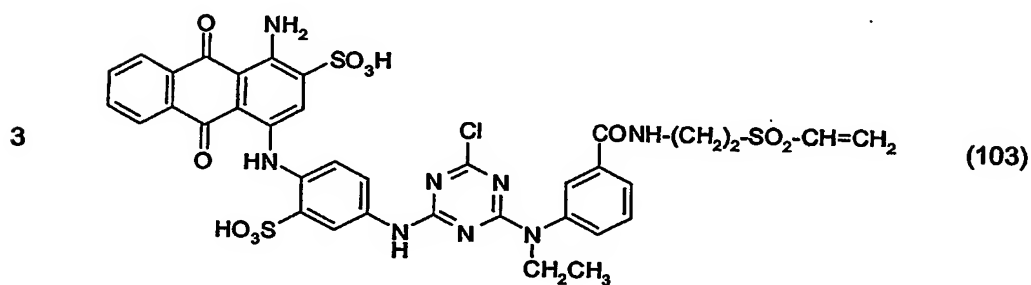
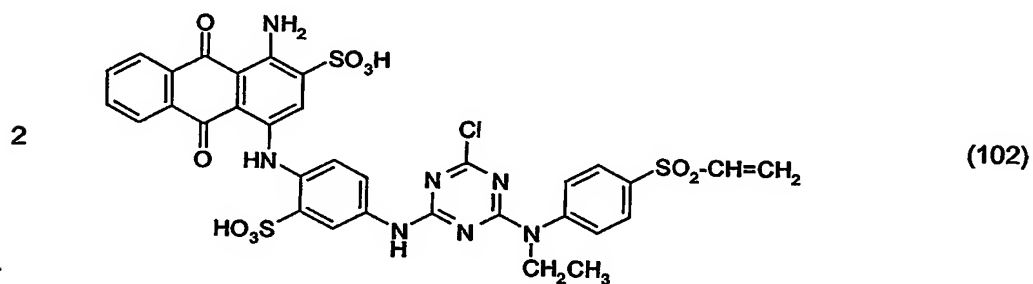
(101).

- 15 -

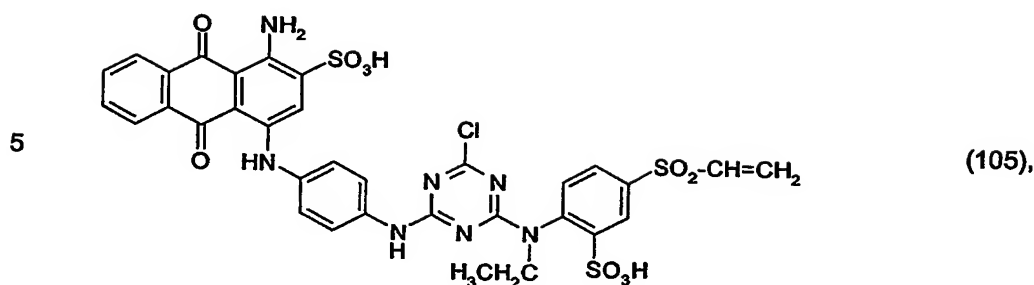
The dye of formula (101) dyes wool and synthetic polyamide fibre material in blue hues.

Examples 2 to 5:

In a manner analogous to that described in in Example 1 it is possible to obtain the dyes of formulae



- 16 -



which dye wool and synthetic polyamide in brilliant blue hues.

Dyeing procedure I:

10 parts of polyamide-6,6 fibre material (Helanca jersey) are dyed in 500 parts of an aqueous liquor that contains 2 g/l of ammonium acetate and is adjusted to pH 5 using acetic acid. The content of dye according to Example 1 is 0.8% based on the weight of the fibre. The duration of dyeing at a temperature of 98°C is from 30 to 90 minutes. The dyed fibre material is then removed and washed and dried as usual. A brilliant blue dyeing having very good fastness properties is obtained.

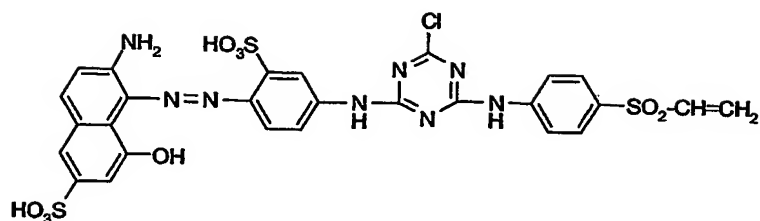
Dyeing procedure II:

10 parts of woollen knitting yarn are stirred at 30°C in a dye bath that contains, per 100 parts of water, 0.8 part of the dye according to Example 1, 0.5 part of sodium sulfate and 2 parts of sodium acetate and that has been adjusted to a pH of 4.5 using acetic acid (80%). The liquor is brought to the boil in the course of 45 minutes and maintained at boiling temperature for a further 45 to 70 minutes. The dyed material is then removed, rinsed thoroughly with cold water and dried. A brilliant blue dyeing having very good fastness properties is obtained.

Process Example 1:

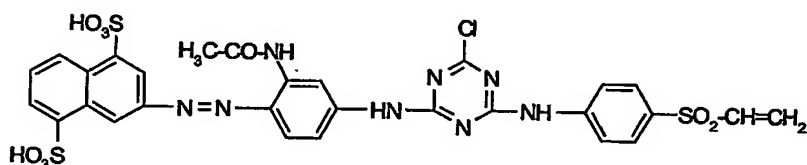
A polyamide-6,6 carpet fabric is dyed continuously from a dye bath containing, per 1000 parts of the dye bath,
 0.46 part of the blue dye of formula (101),
 0.28 part of the red dye of formula

- 17 -



(106) and

0.8 part of the yellow dye of formula



(107)

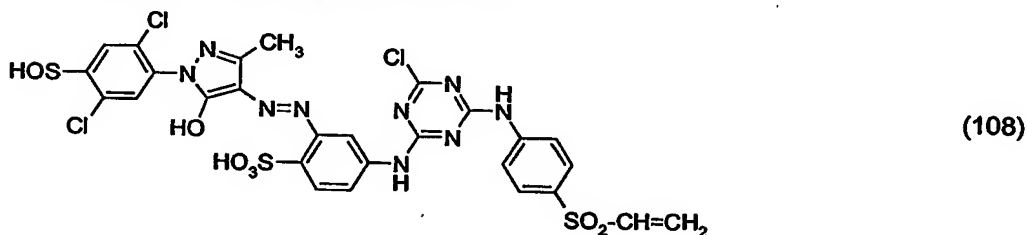
and, in addition, 1.0 part of a commercially available thickener, 3.0 parts of a commercially available antifreeze, 1.0 part of a non-ionic wetting agent, and citric acid in an amount sufficient to establish a pH value of 5.5 in the dye bath. The carpet fabric is then fixed in steam for 5 minutes at 100°C, washed in the usual manner and dried. The carpet fabric is distinguished by a uniform dark-brown dyeing having good fastness properties.

Process Examples 2 and 3: By proceeding as in Process Example 1 but, instead of using 0.46 part of the blue dye of formula (101), 0.28 part of the red dye of formula (106) and 0.8 part of the yellow dye of formula (107), using the reactive dyes indicated below in Table 1, column 2, in the amounts indicated, there are likewise obtained brown dyeings having good levelness and good fastness properties.

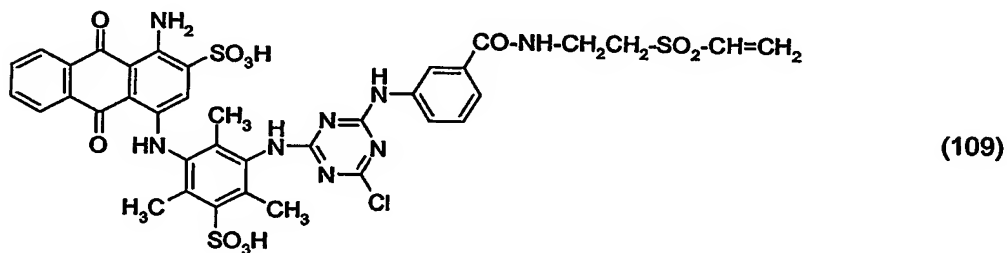
- 18 -

Table 1Ex. Dyes

- 2 0.40 part of the blue dye of formula (101),
0.45 part of the red dye of formula (106) and
0.70 part of the yellow dye of formula



- 3 0.20 part of the blue dye of formula (101),
0.20 part of the blue dye of formula



- 0.45 part of the red dye of formula (101) and
0.42 part of the yellow dye of formula (108)

Process Example 4: In a dyeing apparatus, 100 kg of textured polyamide-6,6 jersey are treated for 10 minutes at 40°C with 2000 litres of liquor containing 4 kg of acetic acid, 0.5 g of wetting agent and 1 kg of a levelling agent. The pH of the liquor is 3.4. There are then added, predissolved in a small amount of water, 430 g of the dye of formula (101) and 440 g of the dye of formula (108).

- 19 -

The material to be dyed is treated in the dye liquor for 5 minutes at 40°C and then heated to 98°C at a heating rate of 1°C/min and dyed at that temperature for 60 minutes. The dyeing is finished in the usual manner. A brilliant green level dyeing having very good fastness properties is obtained.

Process Example 5: In a dyeing apparatus, 70 kg of a fabric of polyamide-6,6 microfibres are treated for 10 minutes at 40°C with 1500 litres of liquor containing 3 kg of formic acid, 0.4 kg of wetting agent and 0.7 kg of a levelling agent. The pH of the liquor is 2.9. There are then added, predissolved in a small amount of water, 700 g of the dye of formula (107), 1300 g of the dye of formula (106) and 430 g of the dye of formula (101). The material to be dyed is treated in the dye liquor for 5 minutes at 40°C and then heated to 110°C at a heating rate of 1°C/min and dyed at that temperature for 60 minutes. The dyeing procedure is followed by an alkaline aftertreatment in order to improve the wet-fastness properties. For that purpose, a fresh bath containing 2 g/l of soda and having a pH of 9.2 is used to treat the dyeing for 20 minutes at 60°C. The dyeing is then rinsed and finished in the usual manner. A level dyeing having excellent fastness properties is obtained.

Process Example 6: The procedure is as described in Process Example 4, except that the alkaline aftertreatment is carried out at 70°C instead of at 60°C.

Process Example 7: The procedure is as described in Process Example 4, except that the alkaline aftertreatment is carried out in a bath containing 5 g/l of soda and 5 g/l of hydrosulfite. The dyeing is treated for 20 minutes at 70°C using that bath.

Process Example 8 (Space dyeing):

A carpet of polyamide-6 yarn is first of all pad-dyed with a liquor containing, per 1000 parts of the liquor, the components indicated below:

0.008 part of the blue dye of formula (101),
0.003 part of the red dye of formula (106),
0.01 part of the yellow dye of formula (107),
3.00 parts of a commercially available thickener,
2.00 parts of a commercially available non-ionic wetting agent,
1.00 part of a commercially available antifreeze,
the pH being adjusted to 5 using the required amount of citric acid.

- 20-

Areas of the dyed carpet are then printed with a printing paste containing, per 1000 parts of printing paste, the components indicated below:

0.50 part of the blue dye of formula (101),
0.50 part of the red dye of formula (106),
15.0 parts of a commercially available thickener,
2.00 parts of a commercially available non-ionic wetting agent,
1.00 part of a commercially available antifreeze,
the pH being adjusted to 5 using the required amount of citric acid.

The dyed and partially printed carpet is then treated with saturated steam for 5 minutes at 100°C, washed in the usual manner and dried, yielding a carpet having red printed areas on a beige-coloured ground, those areas being distinguished by good levelness with good fastness properties.

Process Example 9 (Continuous dyeing): A carpet of polyamide-6,6 yarn is continuously dyed with a liquor containing, per 1000 parts of the liquor, the components indicated below:

0.46 part of the blue dye of formula (101),
0.28 part of the red dye of formula (106),
0.8 part of the yellow dye of formula (107),
1.00 part of a commercially available thickener,
1.00 part of a commercially available non-ionic wetting agent,
3.00 parts of a commercially available antifreeze,
the pH being adjusted to 5.5 using the required amount of citric acid. The dyed carpet fabric is then treated with saturated steam for 5 minutes at 100°C, washed in the usual manner and dried, yielding a carpet distinguished by level dark-brown dyeing with good fastness properties.

- 21 -

Process Example 10 (Displacement printing):

A carpet of polyamide-6,6 yarn is first of all printed with various printing pastes containing the components indicated below, some of which are in varying amounts x, y and z:

x parts of Tectilon® Yellow 3R (Ciba Specialty Chemicals),

y parts of Tectilon® Red 2B (Ciba Specialty Chemicals),

z parts of Tectilon® Blue 4R-01 (Ciba Specialty Chemicals),

x is e.g. 1.05, y 0.34 and z 1.01,

15.0 parts of a commercially available thickener,

10.0 parts of Lyoprint® MP,

2.00 parts of a commercially available non-ionic wetting agent,

1.00 part of a commercially available antifreeze,

the pH being adjusted to 4 using the required amount of citric acid.

The printed carpet is then dyed with a liquor containing, per 1000 parts of the liquor, the components indicated below (the liquor pick-up is 350%):

1.90 parts of the blue dye of formula (101),

0.62 part of the red dye of formula (106),

1.26 parts of the yellow dye of formula (107),

1.00 part of a commercially available thickener,

2.00 parts of a commercially available non-ionic wetting agent,

2.00 parts of a commercially available antifreeze,

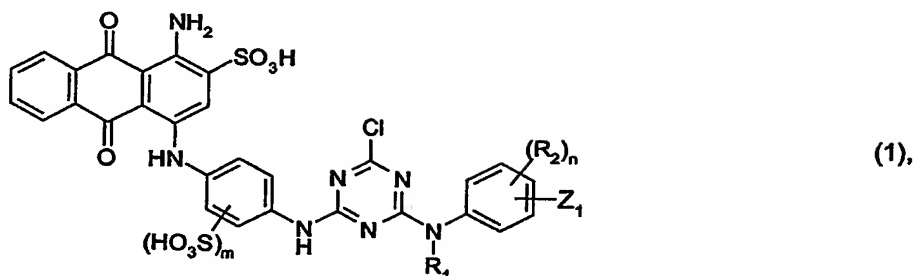
the pH being adjusted to 5.5 using the required amount of citric acid.

The carpet is then treated with saturated steam for 5 minutes at 100°C, washed in the usual manner and dried, yielding a carpet having coloured areas on a dark-violet ground, those areas being distinguished by good levelness with good fastness properties.

- 22 -

What is claimed is:

1. A reactive dye of formula



wherein

R_1 is optionally substituted C_1 - C_4 alkyl,

R_2 is halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy or sulfo,

Z_1 is a radical of formula



wherein

Hal is chlorine or bromine,

Y is vinyl or a radical $-\text{CH}_2\text{CH}_2\text{-U}$ and U is a group removable under alkaline conditions,

k is the number 2, 3, 4, 5 or 6,

n is the number 0, 1 or 2 and

m is the number 0 or 1.

2. A reactive dye according to claim 1, wherein

R_1 is methyl or ethyl, preferably ethyl.

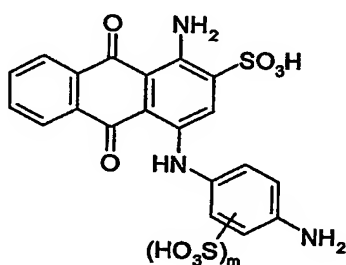
3. A reactive dye according to either claim 1 or claim 2, wherein

Z_1 is a radical of formula (2a) wherein Y is vinyl.

- 23 -

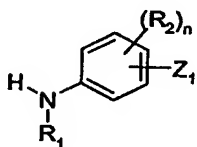
4. A reactive dye according to any one of claims 1 to 3, wherein m is the number 1 and n is the number 0.

5. A process for the preparation of a reactive dye of formula (1), which comprises reacting a compound of formula



(2)

and a compound of formula



(3)

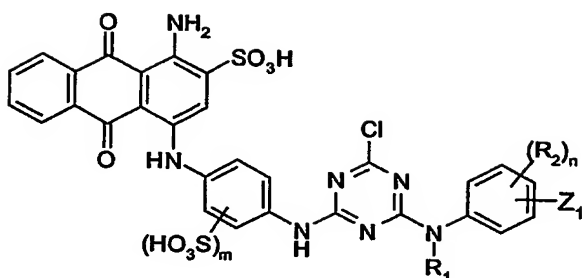
with cyanuric chloride, R_1 , R_2 , Z_1 , m and n being as defined in claim 1.

6. The use of a reactive dye according to any one of claims 1 to 4 or of a reactive dye obtained according to claim 5 in the dyeing or printing of a hydroxyl-group-containing or nitrogen-containing fibre material.

7. Use according to claim 6, wherein a natural or synthetic polyamide fibre material, especially a synthetic polyamide fibre material, is dyed or printed.

8. A process for dyeing or printing a hydroxyl-group-containing or nitrogen-containing fibre material, which comprises using at least one reactive dye of formula

- 24 -



(1),

wherein

R₁ is optionally substituted C₁-C₄alkyl,

R₂ is halogen, C₁-C₄alkyl, C₁-C₄alkoxy or sulfo,

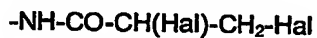
Z₁ is a radical of formula



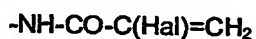
(2a),



(2b),



(2c) or



(2d)

wherein

Hal is chlorine or bromine,

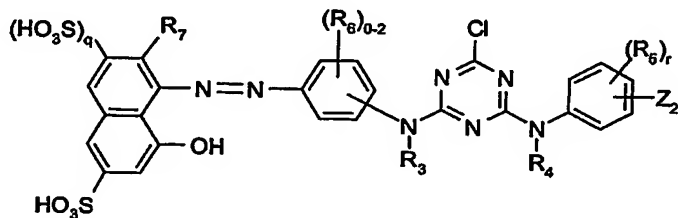
Y is vinyl or a radical $-\text{CH}_2\text{CH}_2-\text{U}$ and U is a group removable under alkaline conditions,

k is the number 2, 3, 4, 5 or 6,

n is the number 0, 1 or 2 and

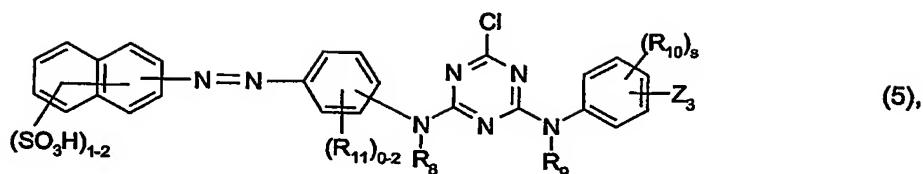
m is the number 0 or 1; together with

at least one reactive dye selected from the group of formulae

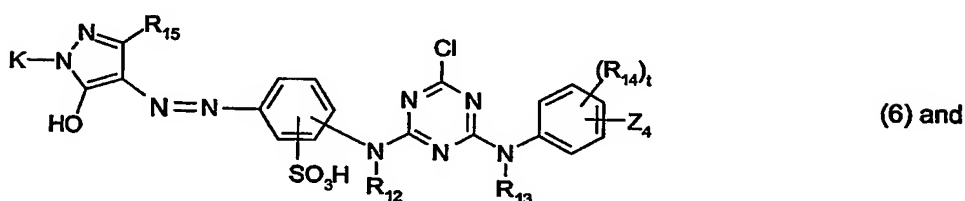


(4),

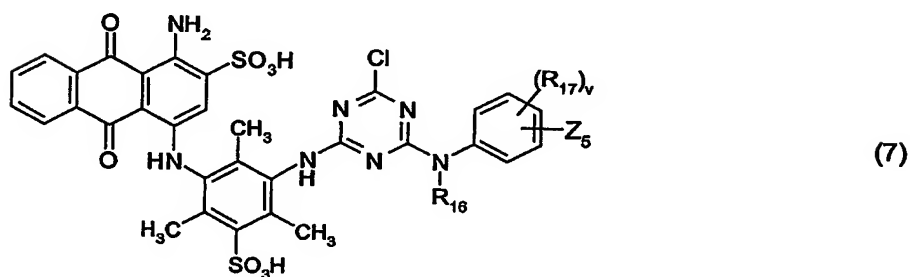
- 25 -



(5),



(6) and



(7)

wherein

R_3 , R_4 , R_8 , R_9 , R_{12} , R_{13} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted C_1 - C_4 alkyl,

R_5 , R_{10} , R_{14} and R_{17} are each independently of the others halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy or sulfo,

$(\text{R}_8)_{0-2}$ and $(\text{R}_{11})_{0-2}$ are each independently of the other 0, 1 or 2 substituents selected from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, ureido, sulfamoyl, halogen, sulfo and carboxy,

R_7 is amino or N-mono- or N,N-di- C_1 - C_4 alkylamino,

R_{15} is C_1 - C_4 alkyl, carboxy, unsubstituted C_1 - C_4 alkoxy or C_1 - C_4 alkoxy substituted by carboxy,

K is a phenyl radical, which is substituted by 0, 1, 2 or 3 substituents selected from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, sulfamoyl, carbamoyl, halogen, sulfo and carboxy, or is a naphthyl radical substituted by 1, 2 or 3 sulfo groups,

Z_2 , Z_3 , Z_4 and Z_5 , each independently of the others, have the definitions given for Z_1 ,

q is the number 0 or 1, and

r , s , t and v are each independently of the others the number 0, 1 or 2.

- 26 -

9. A process according to claim 8, which comprises using at least one reactive dye of formula (1) together with a reactive dye of formula (6), wherein R_1 , R_2 , R_{12} , R_{13} , R_{14} , R_{15} , K , Z_1 , Z_4 , m , n and t are as defined in claim 8.

10. A process according to either claim 8 or claim 9, wherein a natural or synthetic polyamide fibre material, especially a synthetic polyamide fibre material, is dyed or printed.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



10/536679



(43) International Publication Date
17 June 2004 (17.06.2004)

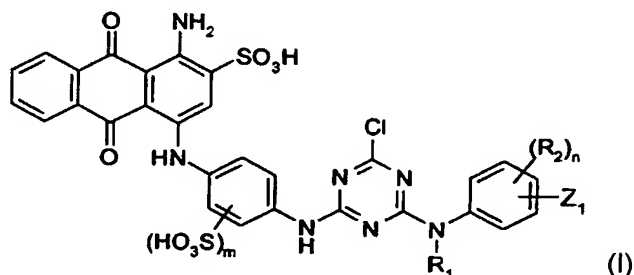
PCT

(10) International Publication Number
WO 2004/050769 A3

- (51) International Patent Classification⁷: C09B 62/445, 67/22
- (21) International Application Number: PCT/EP2003/050878
- (22) International Filing Date: 24 November 2003 (24.11.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 02406046.9 2 December 2002 (02.12.2002) EP
- (71) Applicant (for all designated States except US): CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): SCHMIEDL, Jürgen [DE/DE]; Belchenstrasse 17, 79585 Steinen (DE). SCHOEHN, Damien [FR/FR]; Rue des Sorbiers 7, F-68190 Ensisheim (FR). KOCH, Klaus [DE/CH]; Tramstrasse 35N, CH-4132 Muttenz (CH).
- (74) Common Representative: CIBA SPECIALTY CHEMICALS HOLDING INC.; Patentabteilung, Klybeckstrasse 141, CH-4057 Basel (CH).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- (88) Date of publication of the international search report: 26 May 2005
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/050769 A3

(54) Title: REACTIVE DYES, A PROCESS FOR THEIR PREPARATION AND THEIR USE



(57) Abstract: Reactive dyes of formula (1): wherein R₁ is optionally substituted C₁-C₄alkyl, R₂ is halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy or sulfo, Z₁ is a radical of formula -SO₂-Y (2a), -CO-NH-(CH₂)_k-SO₂-Y (2b), -NH-CO-CH(Hal)-CH₂-Hal (2c) -NH-CO-C(Hal)=CH₂ or (2d) wherein Hal is chlorine or bromine, Y is vinyl or a radical -CH₂CH₂-U and U is a group removable under alkaline conditions, k is the number 2, 3, 4, 5 or 6, n is the number 0, 1 or 2 and m is the number 0 or 1, are suitable for dyeing or printing cellulose-containing fibre materials, preferably natural or synthetic polyamide fibre materials, and produce, with a high colour yield, dyeings and prints having good fastness properties.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/50878

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09B62/445 C09B67/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 247 842 A (CIBA SC HOLDING AG) 9 October 2002 (2002-10-09) Tabelle 3, Herstellungsbeispiel 3 Tabelle 3, Herstellungsbeispiel 4 Tabelle 4, Herstellungsbeispiel 11 Tabelle 4, Herstellungsbeispiel 12 Seite 12, Erläuterungsbeispiel	1-10
Y	DATABASE WPI Section Ch, Week 197813 Derwent Publications Ltd., London, GB; Class E22, AN 1978-23836A XP002239620 -& JP 50 157422 A (NIPPON KAYAKU KK) 19 December 1975 (1975-12-19) abstract page 150, column 2 ----- -/--	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

2 June 2004

Date of mailing of the international search report

16/06/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Ketterer, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/50878

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 631 341 A (KAYANE YUTAKA ET AL) 23 December 1986 (1986-12-23) examples	1-10
A	EP 0 070 807 A (CIBA GEIGY AG) 26 January 1983 (1983-01-26) page 8 page 15 - page 28 page 2, line 1	1-7
A	EP 0 775 776 A (CIBA GEIGY) 28 May 1997 (1997-05-28) examples	1-10
A	US 3 426 018 A (ECKERSLEY DENNIS ET AL) 4 February 1969 (1969-02-04) the whole document	1-7
A	US 5 601 622 A (MUELLER BERNHARD) 11 February 1997 (1997-02-11) claims	1-7
A	US 3 427 308 A (BARBEN IAN KNOWLES ET AL) 11 February 1969 (1969-02-11) claim 2	1-7
A	EP 0 214 093 A (CIBA GEIGY AG) 11 March 1987 (1987-03-11) Seite 94, Verbindung Nr. 360	1-7
P,A	EP 1 325 945 A (CIBA SC HOLDING AG) 9 July 2003 (2003-07-09) the whole document	1-10

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/50878

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1247842	A	09-10-2002	CN 1158926 A	10-09-1997
			DE 59610025 D1	06-02-2003
			EP 1247842 A1	09-10-2002
			EP 0775776 A2	28-05-1997
			JP 9176510 A	08-07-1997
			US 5944855 A	31-08-1999
			US 5779740 A	14-07-1998
JP 50157422	A	19-12-1975	NONE	
US 4631341	A	23-12-1986	JP 1744414 C	25-03-1993
			JP 4032868 B	01-06-1992
			JP 59215361 A	05-12-1984
			JP 59217765 A	07-12-1984
			JP 1773443 C	14-07-1993
			JP 4060146 B	25-09-1992
			JP 60092357 A	23-05-1985
			CH 659078 A5	31-12-1986
			DE 3419072 A1	29-11-1984
EP 0070807	A	26-01-1983	DE 3263888 D1	04-07-1985
			DE 3263889 D1	04-07-1985
			DE 3272886 D1	02-10-1986
			EP 0070806 A2	26-01-1983
			EP 0070807 A2	26-01-1983
			EP 0070808 A2	26-01-1983
			JP 58025358 A	15-02-1983
			JP 58025359 A	15-02-1983
			JP 1289670 C	14-11-1985
			JP 58049753 A	24-03-1983
			JP 60014045 B	11-04-1985
EP 0775776	A	28-05-1997	CN 1158926 A	10-09-1997
			DE 59610025 D1	06-02-2003
			EP 1247842 A1	09-10-2002
			EP 0775776 A2	28-05-1997
			JP 9176510 A	08-07-1997
			US 5944855 A	31-08-1999
			US 5779740 A	14-07-1998
US 3426018	A	04-02-1969	GB 1120392 A	17-07-1968
			CH 462995 A	30-09-1968
			DE 1644561 A1	08-04-1971
			FR 1468386 A	03-02-1967
US 5601622	A	11-02-1997	CN 1133321 A	16-10-1996
			EP 0708150 A1	24-04-1996
			ID 21586 A	25-04-1996
			JP 8127729 A	21-05-1996
			SG 33547 A1	18-10-1996
			TW 415961 B	21-12-2000
			US 5718730 A	17-02-1998
US 3427308	A	11-02-1969	GB 1135931 A	11-12-1968
			CH 473873 A	15-06-1969
			DE 1644564 A1	08-04-1971
			FR 1495035 A	15-09-1967

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/50878

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0214093	A	11-03-1987	BR 8606825 A	27-10-1987
			WO 8701123 A1	26-02-1987
			DE 3667998 D1	08-02-1990
			EP 0214093 A1	11-03-1987
			JP 7064997 B	12-07-1995
			JP 63500667 T	10-03-1988
			KR 9507219 B1	04-07-1995
			US 4786721 A	22-11-1988
			ZA 8606117 A	25-03-1987
EP 1325945	A	09-07-2003	EP 0922735 A1	16-06-1999
			EP 1325945 A2	09-07-2003
			BR 9805323 A	14-12-1999
			DE 59809017 D1	21-08-2003
			ES 2202786 T3	01-04-2004
			JP 11263922 A	28-09-1999
			PT 922735 T	28-11-2003
			TW 446734 B	21-07-2001
			US 6063137 A	16-05-2000
			US 6241789 B1	05-06-2001
			US 2001013149 A1	16-08-2001